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## (54) RADIAL TIRE FOR HEAVY-DUTY VEHICLE

### (57)Abstract:

PROBLEM TO BE SOLVED: To provide a radial tire for a heavy-duty vehicle having heat resistance and cracking resistance while maintaining high elasticity even in long-time vulcanization.

SOLUTION: The radial tire for the large vehicle comprises a belt layer consisting of steel cords and a steel cord coating rubber, the coating rubber comprising a rubber composition compounding a rubber component formed of an isoprene rubber and transpolybutadiene and 1,6-hexamethylene dithioic sodium sulfate dihydrate wherein 1,6-hexamethylene dithioic sodium sulfate dihydrate is compounded with transpolybutadiene of the rubber component at 30% or less of its weight.

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]****[0001]**

**[Field of the Invention]** This invention relates to the radial-ply tire for large-sized cars, especially the radial-ply tire for large-sized construction cars. Especially this invention relates to the radial-ply tire for large-sized cars and the radial-ply tire for large-sized construction cars which raised endurance.

**[0002]**

**[Description of the Prior Art]** The following two points are required of this coating rubber of the radial-ply tire for large-sized cars which has the belt layer which consists of coating rubber of a steel code and this steel code at least. That is, they are the high elasticity which needs \*\* of the belt accompanying radial structure for the tire configuration reservation by the bundle, and the crack-proof growth nature for the improvement in endurance of a tire. These two engine performance has been offered by controlling the degree of sulfur bridge formation of coating rubber, and the carbon black addition to this rubber conventionally.

**[0003]**

**[Problem(s) to be Solved by the Invention]** However, the further enlargement is called for also for the tire used for it with enlargement of a car, especially a construction car these days. If a tire is enlarged, the vulcanizing time in a tire production process will turn into long duration. In this case, when using the conventional sulfur cross-linking method especially, since thermal resistance is inadequate, aggravation of the coating rubber engine performance, especially decline in an elastic modulus may be caused.

**[0004]** On the other hand, even if it vulcanizes long duration by making the addition of bulking agents, such as carbon black, increase, it is known that decline in an elastic modulus can be suppressed. However, this approach reduces the febrility-proof of a rubber constituent, and we are anxious about the increment in failure of the tire resulting from generation of heat. Although similarly decline in an elastic modulus can be suppressed by increasing the quantity of a vulcanization accelerator, the crack-proof growth nature and/or endurance of a tire are made to fall.

**[0005]** Then, the purpose of this invention is to solve the above-mentioned technical problem. Specifically, the purpose of this invention is to offer the radial-ply tire for large-sized cars which has the belt layer which consists of rubber-steel code complex which has the coating rubber which maintains high elasticity also with vulcanization of long duration, and has febrility-proof and crack-proof growth nature, and this rubber, and/or the rubber constituent and steel code of this invention.

**[0006]**

**[Means for Solving the Problem]** In order to solve the above-mentioned technical problem, as a result of this invention persons' inquiring wholeheartedly, it hit that the obtained rubber constituent had the crack-proof growth nature which was excellent even if it performed long duration vulcanization on an idea of a header and the following invention by using together transformer polybutadiene, and 1 and 6-hexamethylene dithio sodium sulfate and dihydrate which are a heat-resistant cross linking agent, and using this heat-resistant cross linking agent by a certain specific ratio.

**[0007] <1>** It is the radial-ply tire for large-sized cars which has the belt layer which consists of coating

rubber of a steel code and this steel code. Said coating rubber It comes to blend rubber component; [ which consists of polyisoprene rubber and transformer polybutadiene ] and 1, and 6-hexamethylene dithio sodium sulfate, and dihydrate. this -- the radial-ply tire for large-sized cars characterized by the loadings of 1 and 6-hexamethylene dithio sodium sulfate and dihydrate consisting of a rubber constituent which is 30% or less of the weight of the transformer polybutadiene in said rubber component.

[0008] <2> In the above <1>, it is good that 1 and 6-hexamethylene dithio sodium sulfate and dihydrate are per [ 0.3 ] rubber component 100 weight section - the 2.0 weight sections.

<3> As for coating rubber, in the above <1> or <2>, it is good that the tensile stress at the time of 100% expanding is more than 3.5MPa(s) (megger pascal) after vulcanization, and tandelta when measuring under conditions of 2% of distortion at 25 degrees C is 0.200 or less.

[0009] <4> As for transformer polybutadiene, in either of above-mentioned <1>- <3>, it is good that the transformer coupling content is 82-98-mol %, and weight average molecular weight is 30,000 to 200,000.

[0010] <5> rubber component; [ which is the rubber constituent used for the coating rubber for steel codes, and consists of polyisoprene rubber and transformer polybutadiene ] and 1, and 6-hexamethylene dithio sodium sulfate, and dihydrate -- blending -- becoming -- this -- the above-mentioned rubber constituent characterized by the loadings of 1 and 6-hexamethylene dithio sodium sulfate and dihydrate being 30% or less of the weight of said transformer polybutadiene.

[0011] <6> In the above <5>, it is good that the loadings of 1 and 6-hexamethylene dithio sodium sulfate and dihydrate are per [ 0.3 ] rubber component 100 weight section - the 2.0 weight sections.

<7> In the above <5> or <6>, it is good that the tensile stress at the time of 100% expanding is more than 3.5MPa(s) (megger pascal) after vulcanization, and tandelta when measuring under conditions of 2% of distortion at 25 degrees C is 0.200 or less.

[0012] <8> As for transformer polybutadiene, in either of above-mentioned <5>- <7>, it is good that the transformer coupling content is 82-98-mol %, and weight average molecular weight is 30,000 to 200,000.

<9> rubber component; [ which it is the rubber-steel code complex which consists of a rubber constituent and a steel code, and this rubber constituent becomes from polyisoprene rubber and transformer polybutadiene ] and 1, and 6-hexamethylene dithio sodium sulfate, and dihydrate -- blending -- becoming -- this -- the above-mentioned complex whose loadings of 1 and 6-hexamethylene dithio sodium sulfate and dihydrate are 30% or less of the loadings of the transformer polybutadiene in said rubber component.

[0013]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail. This invention relates to the radial-ply tire for large-sized cars which has the belt layer which consists of coating rubber of a steel code and this steel code. Next, the coating rubber used for a belt layer is explained first.

[0014] The coating rubber used for this invention comes to blend a rubber component, and 1 and 6-hexamethylene dithio sodium sulfate and dihydrate (for it to be hereafter written as "HTS"). Among these, a rubber component consists of polyisoprene rubber and transformer polybutadiene. Although the polyisoprene rubber used for this invention can use all the natural rubber and synthetic polyisoprenes which can generally come to hand, it is desirable to use natural rubber. As for polyisoprene rubber, it is good among the rubber component 100 weight section 90 - 99 weight section and that it is 95 - 99 weight section preferably.

[0015] As for the transformer polybutadiene used for this invention, it is desirable that the transformer coupling content is 82-98-mol %, and it is good that it is 86 - 98% more preferably. The inclination which makes high the facilitatory effect of elongation crystallinity of polyisoprene rubber arises, so that this transformer coupling content is high. On the other hand, if this content is too low, the facilitatory effect of elongation crystallinity of polyisoprene rubber is not acquired enough, and it is not desirable. In addition, that to which this content exceeds 98-mol % is difficult on composition.

[0016] Moreover, as for the weight average molecular weight of this transformer polybutadiene, it is

good that it is 5x10<sup>4</sup> to 15x10<sup>4</sup> preferably [ that it is 3x10<sup>4</sup> to 20x10<sup>4</sup> ] and more preferably. When molecular weight is in this range, the physical-properties balance at the time of the workability at the time of un-vulcanizing [ of the rubber constituent for coating rubber ] and vulcanization is good. When there is an inclination for an elastic modulus to fall, on the other hand when molecular weight becomes low, and molecular weight becomes high, there is an inclination for workability to fall.

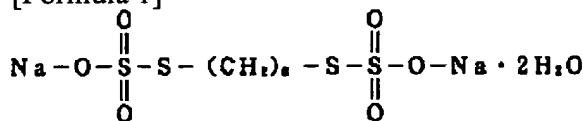
[0017] Furthermore, as for the loadings of transformer polybutadiene, it is good that it is 1 - 5 weight section preferably [ that it is 1 - 10 weight section ] among the rubber component 100 weight section and more preferably. When there are few loadings, there is an inclination for the heat-resistant amelioration effectiveness by long duration vulcanization to become small. Moreover, there is an inclination for the workability at the time of un-vulcanizing [ of the rubber constituent for coating rubber ] to fall. On the other hand, when loadings increase, there is an inclination for febrility-proof to fall. Moreover, fault -- the amelioration effectiveness of the crack-proof growth nature of vulcanized rubber that compatibility with polyisoprene rubber falls is not fully acquired -- may arise.

[0018] Even if a commercial item is used for the transformer polybutadiene used by this invention, what was obtained by composition may be used for it. If the manufacture approach is illustrated, the approach of contacting a butadiene monomer for a nickel BOROASHI rate, tributyl aluminum, triphenyl phosphite, and the 4 yuan system catalyst of trifluoroacetic acid, and carrying out a polymerization in a solvent, can be mentioned. As long as a rubber component is range which does not affect the effectiveness of this invention, it may contain other rubber. As other rubber, it is desirable that it is diene system rubber, such as SBR and other BR.

[0019] Moreover, the coating rubber used for this invention comes to blend 1 and 6-hexamethylene dithio sodium sulfate and dihydrate (HTS) expressed with the following formulas. In addition, HTS is known as a heat-resistant cross linking agent, in order to give the stable structure of cross linkage thermally as compared with sulfur bridge formation.

[0020]

[Formula 1]



[0021] The amount of HTS must be 30 or less % of the weight of the weight of the transformer polybutadiene contained in a rubber component. Moreover, as for the amount of HTS, it is desirable that it is the 0.3 - 2.0 weight section to the rubber component 100 weight section, and it is still more desirable that it is 0.3 - 1 weight section. When the amount of HTS increases, there is an inclination for crack-proof growth nature to fall, and the inclination which remains in the rubber constituent after vulcanization while HTS has been unreacted arises, consequently the stable bridge formation gestalt which is the description of HTS is generated, and the effectiveness which raises heat-resistant aging nature may be spoiled. On the other hand, when the amount of HTS(s) decreases, the depressor effect of the fall of febrility-proof by long duration vulcanization is not sometimes enough.

[0022] The coating rubber used for this invention can contain the various components usually used in the rubber industry other than the above-mentioned rubber component and HTS as this constituent for rubber. For example, additives, such as bulking agent (they are inorganic bulking agents, such as calcium-carbonate and calcium carbonate, to reinforcement nature bulking agent; lists, such as carbon black and silica); vulcanization-accelerator; antioxidant; zinc-oxide; stearin acid; softener; and anti-ozonant, can be mentioned as various components. In addition, the vulcanization accelerator of guanidine systems, such as DPG (diphenylguanidine), etc. can be mentioned to thiuram system vulcanization-accelerator; lists, such as thiazole system vulcanization-accelerator, TT (tetramethylthiuram monosulfide), such as M (2-mercaptopbenzothiazole), DM (dibenzothiazyl disulfide), and CZ (N-cyclohexyl-2-benzothiazyl sulfenamide), as a vulcanization accelerator.

[0023] The rubber constituent of this invention is good to have the following properties. That is, it is good after vulcanization that the tensile stress at the time of 100% expanding is 3.5-4.0MPa preferably

more than 3.5MPa(s) (megger pascal). In addition, measurement of tensile stress can be measured based on JIS K6251-1993. If the above-mentioned tensile stress becomes small, distortion of the belt layer at the time of the constant stress which is an input of a belt layer will be increased, and the inclination which causes the fall of crack-proof growth nature will arise.

[0024] Moreover, as for tandelta when measuring under conditions of 2% of distortion at 25 degrees C, it is [ 0.200 or less ] preferably good [ the rubber constituent of this invention ] 0.16 to 0.2 and that it is 0.18-0.2 more preferably. In addition, tandelta is the index of hysteresis-loss nature, it is high hysteresis-loss nature and its calorific value increases, so that tandelta is large. That is, when tandelta becomes large, it is in the inclination for the febrility-proof of belt coating rubber to fall. In addition, measurement of tandelta can be performed on the conditions of frequency:52Hz for example, using viscoelasticity measuring devices (spectrometer by the Oriental energy machine company etc.).

[0025] The rubber-steel code complex of this invention can be obtained by covering the rubber constituent of this invention in a steel code with a conventional method. The quality of the material of the steel code used, especially structure, etc. are not restricted, but can be suitably chosen from what is usually used according to an application. The rubber-steel code complex of this invention can be used suitable [ the belt layer of for example, the various tires for cars, a carcass layer, a toe of bead, an insertion, a chafer, etc. ] for other industrial use articles.

[0026] The radial-ply tire for large-sized cars of this invention can be manufactured by having the belt layer which consists of the rubber constituent and steel code of this invention, for example, using the rubber-steel code complex of this invention for a belt layer.

[0027] In addition, the belt layer of this invention may have other layers other than the above-mentioned steel code and coating rubber. Although it is desirable that they are a large-sized car and the tire used especially for a large-sized construction car as for the radial-ply tire of this invention, it may be a tire used for other cars.

[0028]

[Example] Hereafter, although this invention is concretely explained using an example, this invention is not limited to an example.

[0029] (Preparation of transformer polybutadiene) It dried, and cyclohexane 300g and 1,3-butadiene 50g were poured into the proof-pressure glassware of 800cm<sup>3</sup> by which the nitrogen purge was carried out, and lanthanum tris (nonyl phenoxide) 0.3mmol was added to it at this. After adding n-butyl lithium 0.9mmol following this, the polymerization was performed at 50 degrees C for 2 hours. From polymerization initiation to termination, the polymerization system was not seen but precipitate's was completely transparent to homogeneity. The polymerization invert ratio was about 95%. Some polymerization solutions were sampled, isopropanol was added, the solid was dried, and the polymer of white powder was obtained.

[0030] Then, 3 was further added for the polymerization system 0.5cm of 5 % of the weight solutions of isopropanols of 2,6-di-t-butyl-p-cresol, the reaction was suspended, and the polymer of transformer polybutadiene was obtained by drying according to a conventional method further. This polymer had 1 and 4-transformer content:92%; and 1, and a 2-vinyl content:5% microstructure, and had molecular weight Mw:6.4x104 and molecular-weight-distribution Mw/Mn:1.3.

[0031] (They are the example 1 of a comparison - the example 8 of a comparison to an example 1 and 2 lists) According to the presentation given in Table 1, each component was kneaded, vulcanization was performed for 60 minutes at 145 degrees C, and the physical properties of the obtained vulcanizate were evaluated. In addition, what was obtained by \*\*\*\* was used for TR-BR. On the occasion of evaluation, the tensile stress at the time of the following 1100% expanding, 2tandelta, and crack-proof [ 3 ] growth nature were measured. Next, each Measuring condition etc. is indicated.

[0032] 1) the JIS No. 3 test piece was created from the tensile stress profit \*\*\*\* vulcanizate at the time of 100% expanding, and it measured according to JIS K 6251-1993.

[0033] 2) About the test piece of the vulcanizate tandelta Obtained, it measured using the viscoelasticity measuring device (spectrometer by the Oriental energy machine company) under with; with a temperature of 25 degrees C a frequency [ distortion 2%; and the frequency of 52Hz ] conditions.

[0034] 3) As a crack-proof growth nature sample, the configuration was started to the No. 3 test piece (JIS#3) of a dumbbell mold. The creep tester (Shimadzu make) performed the constant stress mode test using this sample. Namely, a test-condition:repeat tension-test; load:1.5kg; frequency: It was 5Hz. The value of the examples 2-8 of a comparison was indicated by the characteristic at examples 1 and 2 and a list, having used the result of the example 1 of a comparison as 100 for the count of repeat \*\*\*\* to the fracture in that case. Both the measurement results of these above 1-3 are also shown in Table 1. In addition, the value of one is written as "100%MOD" among Table 1.

[0035]

[Table 1]

表1. タイヤ組成及びその特性

		比較例 1	比較例 2	比較例 3	比較例 4	比較例 5	比較例 6	比較例 7	比較例 8	実施例 1	実施例 2
組成 量部	天然ゴム	100	100	100	100	100	99	85	97	97	95
	TR-BR	—	—	—	—	—	1	15	3	3	5
	カーボン ブラック*1	55.0	50.0	50.0	50.0	50.0	50.0	45.0	50.0	50.0	50.0
	老化防止剤*2	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	接着ゴム一タ-*3	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	亜鉛華	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0
	加硫促進剤*4	0.5	0.5	1.0	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	イオウ	5.0	7.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
	HTS	—	—	—	0.2	2.5	—	—	1.2	0.5	1.1
	HTS/TR-BR 重量比	—	—	—	—	—	—	—	0.40	0.17	0.22
	100%MOD	3.7	3.3	3.7	3.4	3.8	3.3	3.7	4.2	3.9	4.1
	Tan δ	0.205	0.186	0.183	0.180	0.184	0.188	0.211	0.196	0.191	0.196
	耐電脳生長性	100	72	53	92	103	96	117	107	163	170

\* 1 : N 3 3 0

\* 2 : ノクラック 6 C (大内新興化学工業(株) 製)

\* 3 : マノポンド (ローディア社製)

\* 4 : ノクセラーダ Z (大内新興化学工業(株) 製)

[0036] It turns out that crack-proof growth nature of examples 1 and 2 is improving remarkably so that clearly from Table 1.

[0037]

[Effect of the Invention] The radial-ply tire for large-sized cars which has the belt layer which has the coating rubber which maintains high elasticity also with prolonged vulcanization, and has febrility-proof and crack-proof growth nature by this invention, and this rubber, and/or this belt layer can be offered.

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[Translation done.]